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(21) International Application Number: PCT/US88/02576 (22) International Filing Date: 29 July 1988 (29.07.88) (31) Priority Application Numbers: 081,252 150,791 219,630 (32) Priority Dates: 3 August 1987 (03.08.87) 1 February 1988 (01.02.88) 15 July 1988 (15.07.88) (33) Priority Country: US (71) Applicant: EASTMAN KODAK COMPANY [US/US]; 343 State Street, Rochester, NY 14650 (US). (72) Inventors: GUSTAFSON, Bruce, Leroy ; 831 Sir Echo Drive, Kingsport, TN 37663 (US). WEHNER, Paul, Sherman ; 4017 Lakewood Drive, Kingsport, TN 37663 (US). MERCER, Patricia, Lee, Nixon ; 5039 Dublin Road, Kingsport, TN 37664 (US). NELSON, Gregory, Otis ; 1136 Olympus Drive, Kingsport, TN 37663 (US).		(74) Agent: REITER, Stephen, E.; 343 State Street, Rochester, NY 14650 (US). (81) Designated States: AU, DE (European patent), FR (European patent), GB (European patent), IT (European patent), JP, KR, NL (European patent). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: LOW PRESSURE CATALYTIC HYDROGENATION OF CARBONYL-CONTAINING COMPOUNDS AND CATALYSTS THEREFOR (57) Abstract Process for the hydrogenation of carbonyl-containing compounds at mild conditions of temperature and pressure to produce alcohols is disclosed, employing palladium and zinc-containing catalysts. Methods for the preparation of the palladium and zinc-containing catalysts useful for the desired reductive conversion are also disclosed.		

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DescriptionLOW PRESSURE CATALYTIC HYDROGENATION OF
CARBONYL-CONTAINING COMPOUNDS
AND CATALYSTS THEREFOR

5 This invention relates to catalytic hydrogenation. In one aspect, the present invention relates to a process for the selective reduction of carbonyl-containing compounds to alcohols. In another aspect, the present invention relates to catalysts useful for
10 the selective reduction of carbonyl-containing compounds to alcohols, and methods for preparing such catalysts.

 The catalytic hydrogenation of carbonyl-containing compounds, e.g., esters, to produce their
15 corresponding alcohols, is potentially of great commercial value. Catalysts traditionally employed for such conversions include copper chromite based materials, frequently containing a promoter such as barium. Unfortunately, these catalysts typically
20 require high pressure to achieve commercially attractive reaction rates for the hydrogenation of esters, i.e., pressures in excess of 3000 psig. In addition, chromium and barium present toxicity and environmental concerns which must be dealt with if one is to
25 economically and safely use these materials on a commercial scale.

 More recently, substantial amounts of research have been carried out in efforts to develop hydrogenation catalysts capable of reducing carbonyl-
30 containing compounds, e.g., organic acids and esters, to alcohols at reduced pressures. While such catalysts are capable of promoting the hydrogenation of carbonyl-containing compounds to produce alcohols, one problem with such materials is the need to run at

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very low liquid hourly space velocities in order to achieve suitably high conversion levels.

Another problem frequently encountered with such prior art low pressure catalyst systems when employed for the reduction of carbonyl-containing compounds such as aldehydes and ketones, is their lack of selectivity to the desired alcohol product, such catalysts frequently being too active and thus producing product which results from reaction of substrate with additional hydrogen.

Yet another problem encountered with such prior art low pressure catalyst systems, such as Raney nickel, is the ease of handling of such catalysts, which are frequently pyrophoric, and thus require special handling to avoid fire hazard.

Objects of the Invention

An object of the present invention, therefore, is a process for the low pressure, high selectivity, high activity hydrogenation of carbonyl-containing compounds to produce alcohols.

Another object of the present invention is a catalyst system which is capable of promoting the hydrogenation of carbonyl-containing compounds at low reaction pressures.

Still another object of the present invention is a catalyst system which is capable of promoting the hydrogenation of carbonyl-containing compounds at low reaction pressure, which catalyst system is readily prepared and requires no special handling precautions.

These and other objects of the present invention will become apparent from inspection of the detailed description and the appended claims which follow.

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Statement of the Invention

In accordance with the present invention, it has been discovered that palladium supported on zinc oxide is an effective catalyst for the low pressure hydrogenation of carbonyl-containing compounds to selectively produce alcohols in high yield.

In accordance with a particular embodiment of the present invention, it has been discovered that palladium and zinc supported on a carrier is an effective catalyst for the low pressure hydrogenation of carbonyl-containing compounds to selectively produce alcohols in high yield.

In accordance with another embodiment of the present invention, it has been discovered that a catalyst prepared by first depositing palladium on a support, then reducing the palladium sufficiently to "stabilize" the palladium on the support, and then contacting the palladium-treated support with zinc is exceptionally effective for the low pressure hydrogenation of carbonyl-containing compounds to selectively produce alcohols in high yield.

The invention hydrogenation process employs readily prepared, easily handled catalysts and enables a commercially important reaction, i.e., the conversion of carbonyl-containing compounds to alcohols, to be carried out at low reaction pressures, thereby reducing the cost of equipment required for the desired hydrogenation reaction and reducing the safety risks involved in such conversions.

Detailed Description of the Invention

In accordance with the present invention there is provided a method for preparing high activity, low

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pressure hydrogenation catalysts comprising palladium on zinc oxide, which method comprises:

- 5 (a) contacting said zinc oxide support or a precursor thereof with palladium or a reducible compound thereof;
- (b) optionally calcining the resulting palladium-treated zinc oxide support or precursor thereof in the presence of an oxygen-containing gas at a temperature in
10 the range of 200 up to 400°C for a time sufficient to remove substantially all of the counter-ions associated with said palladium or reducible compound thereof and said zinc oxide support or precursor
15 thereof; and
- (c) contacting the optionally calcined palladium-treated zinc oxide support with a reducing atmosphere under conditions
20 sufficient to cause reduction of at least a portion of the palladium to less than the +2 oxidation state.

In accordance with the present invention there is also provided a method for preparing supported high activity, low pressure hydrogenation catalysts
25 comprising palladium and zinc on a support, which method comprises:

- (a) contacting said support with at least one of zinc or a reducible compound thereof and palladium or a reducible compound thereof;
- 30 (b) optionally calcining the resulting palladium and/or zinc treated support in the presence of an oxygen-containing gas at a temperature in the range of 200 up to 400°C for a time sufficient to activate said palladium and/or
35 said zinc component;

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- 5 (c) where palladium is employed in step (a), optionally contacting said palladium-treated support with a reducing atmosphere under conditions sufficient to cause reduction of at least a portion of the palladium to less than the +2 oxidation state;
- 10 (d) optionally contacting said support again with at least one member selected from the group consisting of palladium or a reducible compound thereof and zinc or a reducible compound thereof; with the proviso that said support is ultimately contacted with both palladium and zinc;
- 15 (e) optionally calcining the resulting palladium and zinc treated support in the presence of an oxygen-containing gas at a temperature in the range of 200° up to 400°C for a time sufficient to activate said palladium and said zinc component; and thereafter
- 20 (f) contacting the zinc and palladium-treated support with a reducing atmosphere under conditions sufficient to cause reduction of at least a portion of the palladium to less than the +2 oxidation state.

25 As suggested by the above-described method for catalyst preparation, support can be contacted simultaneously with appropriate palladium and/or zinc components; or support can be contacted with one component followed by a subsequent contacting with

30 the other component; or support can be treated via multiple contacting (with optional calcination/-reduction treatments between contacting) with one or both of the palladium and zinc catalyst components.

35 In accordance with the present invention there is further provided a presently preferred method for

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preparing supported high activity, low pressure hydrogenation catalysts comprising palladium and zinc on a support, which method comprises:

- 5 (a) contacting said support with palladium or a reducible compound thereof;
- (b) contacting said palladium-treated support with a reducing atmosphere under conditions sufficient to form highly dispersed, supported zerovalent palladium;
- 10 (c) contacting said supported zerovalent palladium with zinc or a reducible compound thereof; and thereafter
- (d) optionally calcining the resulting palladium and zinc treated support in the presence of
15 an oxygen-containing gas at a temperature in the range of 200° up to 400°C for a time sufficient to remove undesired counter-ions and/or ligands, thereby activating said zinc component.

20 In accordance with another embodiment of the present invention, there is provided a process for the low pressure hydrogenation of carbonyl-containing compounds of specified structure to produce the corresponding alcohols, which process comprises
25 contacting the carbonyl-containing compounds with a catalyst comprising 0.01 up to 20 weight percent palladium on a zinc oxide-containing support in the presence of hydrogen under hydrogenation conditions.

Catalysts employed in one embodiment of the
30 present invention comprise palladium on zinc oxide support. A wide variety of techniques for contacting palladium and zinc oxide are suitable. For example, palladium can be applied directly to preformed zinc oxide employing such techniques as incipient wetness,
35 wet impregnation, metal atom evaporation,

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precipitation, or appropriate precursors of palladium and zinc can be coprecipitated, then calcined to remove the counter ions introduced by the precursor compounds, and, finally, reduced to convert the
5 palladium to an active form.

Catalysts employed in another embodiment of the present invention comprise palladium and zinc on a carrier or support. A wide variety of techniques for contacting support with palladium and zinc are
10 contemplated for use in the practice of the present invention. For example, palladium or a palladium precursor can be applied directly to support employing such techniques as incipient wetness, wet impregnation, ion exchange, metal atom evaporation,
15 precipitation; then zinc or a zinc precursor can be similarly applied to support; or support can be contacted with both zinc and palladium at the same time; or appropriate precursors of palladium and zinc can be coprecipitated in the presence of support, and
20 then calcined and/or reduced to convert the palladium and zinc to an active form.

In accordance with the presently preferred method for preparing supported catalyst, after support has been contacted with palladium or a palladium
25 precursor, and before the support is further treated with zinc, the palladium-treated support is subjected to reducing conditions sufficient to fix the palladium on the support in a highly dispersed and reduced state so that redispersion of the palladium
30 does not occur upon exposure to corrosive zinc species such as nitrates. For example, this can be accomplished by subjecting the palladium-treated support under a hydrogen atmosphere at a temperature in the range of about 25 up to 400°C.

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A wide range of zinc compounds are suitable zinc oxide precursors for use in the practice of the present invention, e.g., zinc nitrate, zinc halides, zinc acetate, zinc carbonate, and the like.

5 When zinc oxide is employed as catalyst support, a variety of zinc oxide compounds can be directly employed as catalyst support. Typically, such preformed zinc oxide materials will contain an impurity content no greater than about 5%. Preferred
10 zinc oxide compounds employed as catalyst support will contain at least 60% zinc oxide by weight, with up to 40% by weight of inert materials such as:

SiO₂,
Al₂O₃, and
15 TiO₂

being employed as inert diluents and as catalyst binders.

When supported catalyst is contemplated for use in the practice of the invention process, a wide
20 range of inorganic materials can be employed as support for the invention Pd/Zn catalyst. Exemplary materials are relatively non-acidic in that they do not promote significant levels of such undesired side reaction as transesterification, alcohol dehydra-
25 tion, ester hydrolysis, and the like. Such materials include silica (SiO₂), titania (TiO₂), carbon (C), rare earth oxides (e.g., La₂O₃, CeO₂), alumina (Al₂O₃), and the like, as well as mixtures of any two or more thereof.

30 The surface area of the catalyst supports employed in the practice of the present invention can vary widely. Preferably, support materials employed in the practice of the invention will have surface

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areas of at least about $1 \text{ m}^2/\text{g}$. Of course, those of skill in the art also recognize that higher surface area materials will generally produce higher activity catalysts than lower surface area catalysts having comparable composition.

When zinc oxide support is prepared by calcination of a precipitated zinc oxide precursor, temperatures in the range of about 200 up to 400°C are generally employed. Such temperature is maintained for a time sufficient to remove substantially all the counter ions introduced by the zinc oxide precursor (and the palladium compound employed) to form the catalyst. Times in the range of about 2 up to 8 hours or longer are generally effective for this purpose.

Suitable sources of palladium are any compounds which are reducible when subjected to reducing conditions. Since many palladium compounds are convertible to the oxide form upon calcination under the above-described conditions, and the oxides of palladium are readily reduced, many palladium compounds are useful for catalyst preparation. Exemplary palladium compounds include the palladium halides, palladium acetate, palladium nitrate, palladium ammine complexes, organometallic complexes of palladium, and the like.

When the palladium and/or zinc components of the invention supported catalyst are provided as precursor moieties, it is preferred to subject the Pd/Zn-treated support to a calcination treatment at temperatures in the range of about 200 up to 400°C. Such temperature is maintained for a time sufficient to activate the zinc and the palladium components used to form the catalyst. Times in the range of

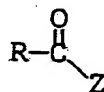
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about 2 up to 8 hours or longer are generally effective for this purpose.

Finally, the Pd/Zn-treated support can optionally be subjected to a reducing atmosphere under conditions sufficient to cause reduction of at least a portion of the palladium to less than the +2 oxidation state.

When the zinc component of the presently preferred supported catalyst (i.e., where palladium is "fixed" on the support before zinc is applied) is provided as a precursor moiety, it is preferred to subject the Pd/Zn-treated support to a calcination treatment at temperatures in the range of about 200 up to 400°C. Such temperature is maintained for a time sufficient to remove undesired counter-ions and/or ligands, thereby activating the zinc component used to form the catalyst. Times in the range of about 2 up to 8 hours or longer are generally effective for this purpose.

The term "carbonyl-containing compounds" as employed in this specification is intended to include compounds of the structure



wherein R is a C₁-C₂₀ alkyl or substituted alkyl radical; or

a C₂-C₂₀ alkenyl or alkynyl radical or substituted derivative thereof;

wherein said substituted groups include ethers, amines, additional carbonyl groups, aryl groups, hydroxyl groups and alkoxy groups; and

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Z=H,

R', wherein R' is defined the same as R, and is selected independently of R,

OR', wherein R' is as defined above,

5 X, wherein X is any one of the halogens, or

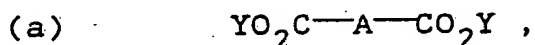
NR''₂, wherein each R'' is independently selected from H or R';

with the proviso that R and Z can be joined as part of a polymethylene or hydrocarbyl- or heteroatom-
10 substituted polymethylene radical,

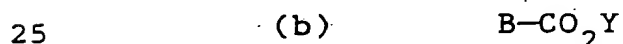
poly-carbonyl analogs of such carbonyl-containing compounds; and

mixtures of any two or more thereof.

Preferred carbonyl-containing compounds are
15 compounds selected from the group consisting of:



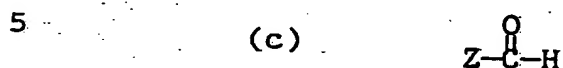
wherein A is an alkylene moiety, an alkenylene moiety, or an alkynylene moiety having 1 up to 20 carbon atoms, or substituted derivative thereof, or a
20 cycloalkyl or cycloalkenyl moiety having 4-12 carbon atoms or substituted derivative thereof; and wherein each Y is independently a C₁ up to C₁₂ alkyl, alkenyl or alkynyl radical or substituted derivative thereof;



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wherein B is an alkyl, alkenyl or alkynyl radical, or substituted derivative thereof, having 1 up to 20 carbon atoms; and

wherein Y is defined as above;



wherein Z is an alkyl, alkenyl or alkynyl radical having 1 up to 20 carbon atoms or substituted derivatives thereof; and

mixtures of any two or more thereof.

- 10 Exemplary carbonyl-containing compounds which satisfy the above formulae include alkyl oleates, dialkyl adipates, propionaldehyde, dialkyl cyclohexane dicarboxylates, alkyl acrylates, alkyl propionates, alkyl isobutyrate, alkyl normal
- 15 butyrates, alkyl acetates, nonanal, dialkyl butane dicarboxylates, alkyl methacrylates, alkyl crotonates, alkyl isocrotonates, alkyl sorbates, alkyl cinnamates, maleic anhydride, alkyl fumarates, dialkyl succinates, succinic anhydride, alkyl
- 20 glutarates, dialkyl malonates, dialkyl octanedioates, dialkyl decanedioates, dialkyl dodecanedioates, alkyl laurates, alkyl myristates, alkyl palmitates, alkyl stearates, alkyl linoleates, alkyl linolenates, alkyl isovalerates, alkyl normal valerates, alkyl
- 25 caproates, alkyl caprylates, alkyl 2-ethylhexanoates, dialkyl cyclohexanedioates, γ -butyrolactone, alkyl phenylacetates, alkyl cyclohexane carboxylates, alkyl pyruvates, alkyl glycolates, alkyl oxalates, alkyl formates, alkyl lactates, alkyl citrates, glyceride
- 30 esters, and the like.

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Typical alkyl groups employed have from 1 up to 20 carbon atoms, with alkyl groups having 1 up to 6 carbon atoms being preferred.

The hydrogenation process of the present invention involves contacting at least one of the above-described carbonyl-containing compounds with at least one of the above-described palladium/zinc oxide catalysts in the presence of hydrogen under hydrogenation conditions. Hydrogenation conditions typically employed in the practice of the present invention are set forth below.

The process of the present invention can be operated in a variety of configurations. Depending on the substrate to be hydrogenated, the preferred method of operation is frequently in a fixed bed flow reaction system. If the vapor pressure of the substrate to be hydrogenated is sufficiently high at reaction temperature, the desired method of operation may be vapor phase, i.e., all reactants and products exist in the gaseous phase. For other substrates, the desired method of operation may be a trickle bed configuration. Regardless of the method of operation, the desired time of contact between the reactants and catalyst components can be varied as desired to achieve the desired level of reaction.

In typical fixed bed operation, pressures in the range of 100-10,000 psig will be employed. Preferably, the pressure will be in the range of 100-2500 psig. Similarly, temperatures in the range of 25-400°C can be used, with a more preferred range of 100-290°C. While the feed rate of the substrate will be varied to control the level of conversion, normal liquid hourly space velocities (LHSV) will be in the range of about 0.01-100 h⁻¹, with a preferred range of 0.1-20 h⁻¹. The molar ratio of

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hydrogen to substrate will typically be in the range of 1:1 to 1000:1 with a preferred range of 2:1 to 100:1.

Alternatively the invention may be conducted in a slurry phase reactor. In slurry phase operation, the ratio of carbonyl-containing compound to catalysts employed can vary widely, with ratios as low as 1:1 or lower being operable, but not economically attractive; and ratios as high as 10,000:1 and higher also being operable, but generally providing relatively low conversions unless very long contact times are employed. Preferred carbonyl-containing compound:catalysts ratios fall within the range of about 1:1 up to 1,000:1, with ratios in the range of about 2:1 up to 100:1 being most preferred because good levels of conversion of the carbonyl-containing compounds are obtained without requiring excessive amounts of catalysts, or extremely long contact times.

While the invention hydrogenation process can be carried out in the absence of solvent, it is presently preferred to perform the process in the presence of a suitable solvent. Suitable solvents are compounds which are fluid and in which the carbonyl-containing starting material is soluble at reaction temperature, and which are non-reactive under hydrogenation conditions. Preferred solvents are those which are fluid and in which the carbonyl-containing starting material is soluble at room temperature. Exemplary solvents include aromatic solvents such as toluene; alcohols such as methanol; ethers such as diphenyl ether and tetrahydrofuran; and the like.

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When employed, the volume/volume ratio of solvent to substrate can vary widely, typically falling in the range of about 5:95 to 95:5.

5 In a preferred embodiment of the present invention, hydrogenation of carbonyl-containing compounds is carried out with small amounts of water (i.e., 0.01 up to about 2 wt. % water based on the total weight of reactants and solvent) present in the reaction mixture. It has been found that selectivity
10 to hydrogenation (as opposed to transesterification between reactant and product) products is greatly improved by the presence of such small quantities of water in the reaction mixture.

Following hydrogenation, the desired product can
15 be recovered and purified using conventional techniques well known to those of skill in the art. For example, catalysts can be removed from the reaction mixture by filtration, decantation and the like. By-products and unreacted starting material as
20 well as solvent, if employed, can be separated from the product by distillation, recrystallization, solvent/solvent extraction, and the like.

The invention will now be described in greater detail by reference to the following non-limiting
25 examples.

EXAMPLE 1 - Catalyst Preparation

a. Pd on ZnO Support

A sample of 1 wt % Pd supported on ZnO was prepared as follows: A solution of Pd was prepared
30 by dissolving 20 g of $\text{Pd}(\text{NO}_3)_2$ in 50 ml of H_2O and 16 g of HNO_3 . This solution was diluted to 750 ml and added to 925 g of powdered ZnO. The resulting mixture was heated at 90°C in air until dry. The

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sample was then calcined at 200°C for two hours prior to catalytic evaluation. Approximately 1 cc of powdered sample was loaded into a plug flow micro-reactor and heated to 300°C in flowing hydrogen. The catalyst was held at 300°C for two hours prior to evaluation for hydrogenation of carbonyl-containing compounds.

b. Pd-Zn on SiO₂ Support

A sample of 1 wt % Pd on Davison Grade 59 SiO₂ was prepared by dissolving 0.48 grams (g) of Pd(NO₃)₂ in 29.4 mL of water and adding the resulting solution to about 20 g of the solid SiO₂ support material. The resulting solid sample was dried in air at 90°C for 30 minutes and then further calcined in air at 350°C for 12 hours. This resulting Pd/SiO₂ catalyst was split into separate fractions for zinc addition. Zinc was added by dissolving the appropriate amount of zinc nitrate in a small amount of water and adding this solution to the Pd/SiO₂ sample. The resulting solid was dried at 90°C in air and then calcined at 200°C for several hours prior to evaluation for hydrogenation of carbonyl-containing compounds.

c. Pd-Zn on SiO₂ with Intervening Reduction of Pd

A sample of 2.8 wt % Pd on Davison Grade 59 SiO₂ was prepared by dissolving 7 grams (g) of [Pd(NH₃)₄]Cl₂ in 25 mL of water and adding the resulting solution to about 100 g of the SiO₂ support material which was suspended in about 2,000 mL of water containing sufficient NH₄OH to adjust the pH to about 11.0. After soaking for about two hours at room temperature, the SiO₂ was recovered by filtration, washed with about 400 mL of

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water, then dried in air at 120°C for about 18 hours and then further treated to reducing conditions as follows:

- 5 (a) 500 standard cubic centimeters per minute (sccm) of argon for about 1 hour at room temperature;
- (b) 500 sccm of argon for an additional 1 hour at 120°C;
- 10 (c) 500 sccm of argon for an additional 1 hour at 260°C;
- (d) argon flow was replaced with hydrogen and catalyst temperature increased; hydrogen flow was maintained for about 1.5 hours after the temperature had reached about 15 400°C; then
- (e) the catalyst was allowed to cool to about 380°C, the hydrogen flow replaced with about 500 sccm of argon, and catalyst then allowed to cool to room temperature under continued 20 argon flow.

The resulting Pd/SiO₂ catalyst was split into separate fractions for zinc addition. Zinc was added by dissolving the appropriate amount of zinc nitrate [Zn(NO₃)₂·6H₂O] in about 50 mL of water and 25 adding this solution to 20 g portions of the Pd/SiO₂ sample. The resulting solid was dried initially by stirring to steam bath temperature, followed by heating to about 120°C in air and then calcined in flowing air at 200°C for 3 hours prior to 30 evaluation for hydrogenation of carbonyl-containing compounds.

EXAMPLE 2 - Methyl Acetate Hydrogenation; Effect of Water in the Feed

Catalyst prepared as described in Example 1a was 35 employed for the vapor phase hydrogenation of methyl

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acetate. All evaluations were conducted using a hydrogen/ester ratio of 4.0 and a gas hourly space velocity (GHSV; volume of gas/volume of catalyst/hr) of 30,180 hr⁻¹. The effect of water content in the feed is demonstrated by the results presented in Table I.

Table I
Catalytic Hydrogenation over Pd/ZnO

Run #	Temp., °C	Pressure, psig	wt % H ₂ O	Rate (μmoles/g-cat sec)*		
				MeOH	EtOH	EtOAc
1	298	730	0.0	7.3	2.0	3.6
2	298	720	0.1	4.3	2.4	1.8
3	298	720	0.5	2.8	1.5	0.3
4	296	725	1.0	1.5	1.1	0.1

*MeOH = methanol

EtOH = ethanol

EtOAc = ethyl acetate

The results set forth in Table I demonstrate that the addition of small amounts of water to the reaction mixture promotes improved catalyst performance by reducing the occurrence of undesired transesterification by-product formation.

EXAMPLE 3 - Hydrogenation of Methyl Acetate

a. Pd on ZnO Catalyst

Catalyst prepared as described in Example 1 was evaluated in the manner described in Example 2. The

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water content of the feed was approximately 1% by weight for all of the runs carried out. Results from these evaluations are presented in Table II:

Table II

Catalytic Evaluation of Pd/ZnO
Methyl Acetate Hydrogenation

Run #	Temp., °C	Press., psig	H ₂ /Ester, moles	Rate (μmoles/g-cat sec)*		
				MeOH	EtOH	EtOAc
5	296	570	0.34	2.1	1.4	<0.01
6	295	735	0.34	2.5	1.8	0.05
7	307	980	0.15	7.1	5.9	0.7
8	333	735	3.97	11.0	9.0	0.8

*MeOH = methanol
EtOH = ethanol
EtOAc = ethyl acetate

The results set forth in Table II demonstrate that Pd/ZnO catalyst is effective for the conversion of esters with high selectivity to the corresponding alcohols at pressures below 1000 psig. In addition, excellent catalyst performance is obtained under a variety of the reaction parameters, i.e., temperature, pressure and feed composition.

b. Supported Pd-Zn Catalysts

Catalysts prepared as described in Example 1b and 1c were employed for the vapor phase hydrogenation of methyl acetate.

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Catalytic evaluations were conducted in a vapor phase micro-reactor system using 1-2 cc of powdered catalyst. Methyl acetate feed was pumped into a heated chamber which was purged with the hydrogen feed gas. Typical GHSV were in the range of 30,000 h⁻¹, with H₂/ester ratios in the range of 3.6 up to 4.5 being typical. Product analysis of exit stream from the reactor was accomplished by gas chromatography. Results obtained at 300°C, 750 psig, at conversions of <20% are presented in Table III.

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Table IIIMethyl Acetate Hydrogenolysis

2.8% Pd-Zn/SiO₂ Catalyst
300°C

700 psig

H₂ /Ester = 3.0

5

		Rate (μmole/g-cat sec)			
Catalyst		MeOH	EtOH	EtOAc	Total*
A. Supported Catalyst Prepared as described in Example 1b:					
10	Pd/SiO ₂	1.21	0.016	0.073	0.089
	Pd-Zn/SiO ₂ (1:1)**	2.74	0.024	0.85	0.87
15	Pd-Zn/SiO ₂ (1:2)**	6.48	0.12	2.25	2.37
	Pd-Zn/SiO ₂ (1:5)**	3.09	0.00	0.84	0.84
	Pd-Zn/SiO ₂ (1:10)**	2.31	0.012	0.68	0.69
20	Zn/SiO ₂	0.00	0.00	0.00	0.00
B. Supported Catalyst Prepared as Described in Example 1c:					
	Pd-Zn (1:0)	21.	3.5	2.1	5.6
	Pd-Zn (1:1)	46.	24.	14.	38.
25	Pd-Zn (1:2)	48.	16.	19.	35.
	Pd-Zn (1:5)	6.7	0.7	2.8	3.5
	Pd-Zn (1:10)	2.6	.08	1.1	1.2

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Table III (Cont'd)

Catalyst	Rate (μ mole/g-cat sec)			
	MeOH	EtOH	EtOAc	Total*
Pd-Zn (1:0)	0.0	0.0	0.0	0.0
5 Comparative Example*** Pd-Zn (1:2)	8.7	3.7	3.1	6.8

MeOH - Methanol, EtOH = Ethanol, EtOAc = Ethyl Acetate

*Total = Rate EtOH + Rate EtOAc

10 **The numbers in parenthesis indicate the atomic ratio of Pd:Zn.

15 ***Catalyst was prepared by treating SiO₂ with NH₄OH and Pd(NH₃)₄Cl₂ (pH = 11.0) for 80 minutes, filtering the solid material from solution, rinsing with water, and drying in air at 120°C for 24 hours. Zinc was added by dissolving an appropriate amount of zinc nitrate in a small amount of water and adding this to the Pd/SiO₂ sample. The resulting solid was dried at 90°C in air and then calcined at 200°C for 20 three hours prior to evaluation for catalytic activity.

25 The results set forth in Table III demonstrate that supporting palladium and zinc on silica results in catalysts with performance superior to the corresponding supported monometallic samples.

C. Catalysts Employed Using Ion-Exchange Technique

A series of catalysts similar to those described in Example 1b were prepared except that the Pd was added using an ion exchange technique and the Pd loading level was 2.8 wt %. The catalysts were prepared by treating the SiO₂ sample with NH₄OH and Pd(NH₃)₄Cl₂ (pH = 11.0) for 80 minutes, filtering the solid material from solution, rinsing

- 23 -

with water, and drying at 120°C for 24 hours. Addition of zinc was accomplished according to the procedure of Example 1. The resulting samples were calcined for about 3 hours at about 200°C prior to evaluation for catalytic activity. Results from this catalytic evaluation using the conditions employed in Example 2 are presented in Table IV.

Table IV
Methyl Acetate Hydrogenation

Catalyst	Rate (μ mole/g-cat sec)			
	MeOH	EtOH	EtOAc	Total*
Pd-Zn (1:0)	3.17	0.02	0.86	0.89
Pd-Zn (1:1)	5.70	3.65	1.35	5.00
Pd-Zn (1:2)	8.72	3.73	3.05	6.78
Pd-Zn (1:5)	4.60	0.41	2.18	2.59
Pd-Zn (0:1)	0.00	0.00	0.00	0.00

MeOH = Methanol, EtOH = Ethanol, EtOAc = Ethyl Acetate
*Total = Rate EtOH + Rate EtOAc

The results set forth in Table IV indicate that catalysts prepared by ion exchange of the palladium component exhibit activity for the low pressure hydrogenation of carbonyl compounds. In addition, it is evident that catalyst performance is dependent on the Pd-Zn ratio. At lower Pd-Zn ratios, selectivity to the alcohol is enhanced, but the overall rate of hydrogenation is lower than observed at higher Pd-Zn ratios. Thus, the Pd-Zn ratio can be used to adjust the rate of hydrogenation.

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D. Effect of Varied Pd Loading Level

A series of catalysts were prepared using the procedure described in Example 3c except that the palladium loading level was varied from 1-5 wt % and the Pd-Zn atomic ratio was held constant at 1:2. These catalysts were evaluated as set forth in Example 2. For comparison, results from a 1% Pd on ZnO supported catalyst described in Example 1a are shown. Data from this latter catalyst were collected under identical conditions except that the total pressure was 730 psig.

Table V
Methyl Acetate Hydrogenation

Catalyst	Rate (μ mole/g-cat sec)			
	MeOH	EtOH	EtOAc	Total*
1% Pd-Zn/SiO ₂	4.2	0.8	1.8	2.6
2.8% Pd-Zn/SiO ₂	8.7	3.7	3.1	6.8
5% Pd-Zn/SiO ₂	30.4	6.0	14.5	20.5
1% Pd/ZnO	7.3	2.0	3.6	5.6

MeOH = Methanol, EtOH = Ethanol, EtOAc = Ethyl Acetate
*Total = Rate EtOH + Rate EtOAc

These results demonstrate that higher palladium loading levels give catalysts having dramatically higher activity for ester hydrogenation.

E. Effect of Water Addition on Supported Pd-Zn Catalyst

Catalyst prepared as described in Example 3d and containing 5 weight % Pd was evaluated as described in Example 3b, except the ester feed (methyl acetate).

- 25 -

was supplemented with 1 weight % (based on the total weight of liquid feed) of water. The results of this experiment and a comparison in which no water was added to the feed are summarized in Table VII.

5

Table VIIEffect of Water on Methyl Acetate Hydrogenation

Weight % Water in Feed	Rate of Formation, μmoles/g-cat sec			
	MeOH	EtOH	EtOAc	Total
10 0.0	30.0	5.0	14.0	19.0
1.0	2.0	1.8	1.2	3.0

In the absence of water, transesterification product, ethyl acetate, represents more than 70% (14 out of 19 moles) of the reaction product; while in the presence of water, transesterification product represents only about 40% of the reaction product. Thus, the presence of water is seen to suppress transesterification and thereby give improved selectivity to the desired direct hydrogenation product.

EXAMPLE 4 - Hydrogenation of Methyl Propionatea. Pd/ZnO Catalyst

The catalyst prepared as described in Example 1a was evaluated in the same manner as described in Example 2 for the hydrogenation of methyl propionate. Reaction parameters and results from this evaluation are given below.

- 26 -

Temperature - 333°C
Pressure - 710 psig
H₂/ester - 4.8
GHSV - 29,178 h⁻¹
Conversion - 16. %

5

Rate (μmoles/g-cat sec): methanol propanol
12. 9.0

These results demonstrate that Pd/ZnO is an effective catalyst for the hydrogenation of methyl propionate to propanol and methanol. Note the very high reaction rates obtained even under non-optimized reaction conditions.

b. Supported Catalyst Prepared as Described in Example 1b:

15 The catalyst prepared as described in Example 3d and containing 5 weight % was used for the hydrogenation of methyl propionate to produce n-propanol, employing the procedure set forth in Example 3b, except that methyl propionate was used instead of
20 methyl acetate.

The conversion of methyl propionate to n-propanol proceeded at a rate of about 14 μmoles/g-cat sec, thereby demonstrating that Pd-Zn/SiO₂ catalyst is effective for the hydrogenation of methyl
25 propionate.

EXAMPLE 5 - Hydrogenation of Methyl n-Butyrate

The catalyst prepared as described in Example 1a was evaluated in the same manner as described in Example 2 for the hydrogenation of methyl
30 n-butyrate. Reaction parameters and results from this evaluation are given below.

- 27 -

Temperature - 333°C
Pressure - 725 psig
H₂/ester - 5.6
GHSV - 28,410 h⁻¹
Conversion - 17. %

Rate (μmoles/g-cat sec): methanol n-butanol
5.9 6.1

The results demonstrate that Pd/ZnO is an effective catalyst for the hydrogenation of methyl n-butyrate to n-butanol and methanol.

EXAMPLE 6 - Hydrogenation of Methyl i-Butyrate

The catalyst prepared as described in Example 1a was evaluated in the same manner as described in Example 2 for the hydrogenation of methyl i-butyrate. Reaction parameters and results from this evaluation are given below.

Temperature - 334°C
Pressure - 725 psig
H₂/ester - 5.7
GHSV - 28,372 h⁻¹
Conversion - 25. %

Rate (μmoles/g-cat sec): methanol i-butanol
2.9 6.0

These results demonstrate that Pd/ZnO is an effective catalyst for the hydrogenation of methyl i-butyrate to i-butanol and methanol. Even under these non-optimized reaction conditions, the per pass conversion was 25%.

EXAMPLE 7 - Hydrogenation of Ethyl Acetate

a. Pd/ZnO Catalyst

The catalyst prepared as described in Example 1a was evaluated in the same manner as described in

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Example 2 for the hydrogenation of ethyl acetate.
Reaction parameters and results from this evaluation
are given below.

5 Temperature - 332°C
 Pressure - 725 psig
 H₂/ester - 4.9
 GHSV - 29,100 h⁻¹
 Conversion - 16. %

10 Rate ($\mu\text{moles/g-cat sec}$): $\frac{\text{Ethanol}}{16.7}$

15 These results demonstrate that Pd/ZnO is an effective catalyst for the hydrogenation of ethyl acetate to ethanol. Note the high selectivity and very high rate of reaction even under these non-optimized conditions.

b. Supported Catalyst Prepared as Described in Example 1b:

20 The catalyst prepared as described in Example 3d and containing 5 weight % Pd was used for the hydrogenation of ethyl acetate according to the procedure set forth in Example 3b, except that ethyl acetate was used instead of methyl acetate.

The conversion of ethyl acetate to ethanol proceeded at a rate of about 30 μ moles/g-cat sec, thereby demonstrating that Pd-Zn/SiO₂ is an effective catalyst for the hydrogenation of ethyl acetate.

EXAMPLE 8 - Hydrogenation of 1,4-Dimethylcyclohexane
Dicarboxylate

30 A catalyst was prepared in the same manner as described in Example 1a. For catalytic evaluation, 260 cc of catalyst (14X40 standard mesh particles) was loaded into a 1 inch fixed bed reactor. The

- 29 -

sample was treated in a hydrogen flow while heating the catalyst to reaction temperature. The system pressure was then increased to the desired reaction pressure. The ester feed consisted of 10 wt% 1,4-dimethylcyclohexane dicarboxylate (DMCD) in 1-dodecanol. Catalytic evaluation was conducted using a liquid feed rate of 80 g/h, 290°C, 1250 psig, and a 1000 standard cubic centimeters (sccm) hydrogen flow. Under these conditions, the DMCD conversion was 93.3%. The observed products were 60 mol % cyclohexanedimethanol (CHDM) and 40 mole % 1-methyl, 4-dodecyl, cyclohexanedicarboxylate.

The above-described catalyst and reaction set-up were employed in the same manner as described except that the reaction conditions were changed to a liquid feed rate of 13 g/h, 300°C, 1250 psig, and 130 sccm hydrogen. Under these conditions, the observed conversion of DMCD was 99.5% with 93.3% molar selectivity to CHDM.

These results demonstrate that Pd/ZnO is a very effective catalyst for the selective hydrogenation of DMCD to CHDM.

EXAMPLE 9 - Effect of Support Surface Area on Catalyst Performance

Catalyst samples were prepared as described in Example 1a except that various sources of ZnO were used for the catalyst support.

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Table VI

Catalytic Evaluation of Pd/ZnO
Methyl Acetate Hydrogenation.

5	Temperature - 300°C Pressure - 720 psig H ₂ /Ester - 4.0 Water - 1 wt %					
10	Run #	ZnO Source	BET Surface Area, m ² /g	Rate (μmoles/g-cat sec)*		
				MeOH	EtOH	EtOAc
	15	A	3.3	3.0	2.4	0.2
	16	B	4.7	2.8	2.0	0.2
	17	C	4.3	2.8	2.3	0.1
15	18	D	27.0	6.0	5.8	0.4

*MeOH = methanol

EtOH = ethanol

EtOAc = ethyl acetate

These results demonstrate that a variety of zinc oxide-containing support materials are useful supports for the Pd/ZnO catalyst of the present invention. In addition, the results show that the rate of reaction with Pd/ZnO catalyst is greatly improved with higher surface area support.

25 EXAMPLE 10 - Catalyst with Modified Catalyst Support:
ZnO/Al₂O₃

ZnO/Al₂O₃ was prepared by dissolving 365 g of zinc nitrate in 800 ml of water at 60°C. A solution of Na₂CO₃ (160 g/700 ml) was slowly added to the Zn solution while stirring to precipitate the Zn.

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The resulting precipitate was washed in 1000 ml of water, filtered and dried at 90°C. The resulting solid was heated in a flow of air at 350°C for four hours. A portion of this solid (50 g) was added to 32 g of aluminum hydrate and 200 ml of water. This mix was blended for 20 minutes, filtered, and finally heated in a flow of air at 350°C for four hours. The resulting powder had a BET surface area of 79 m²/g. The final Pd/ZnO, Al₂O₃ catalyst was prepared by adding an aqueous solution containing 0.24 g of Pd nitrate to 10 g of the ZnO/Al₂O₃ support material, drying the resulting mixture at 90°C, and then heating in a flow of air at 250°C for four hours.

The catalyst was evaluated for methyl acetate hydrogenation activity as described in Example 2. The reaction parameters employed and results obtained were as follows:

Temperature - 332°C
Pressure - 720 psig
H₂/ester - 4.1
Wt% H₂O - 0.0
GHSV - 30,180 h⁻¹
Methyl Acetate conversion - 12.0%

Product	Rate (μmoles/g-cat sec)
CH ₃ OH	21.4
CH ₃ CH ₂ OH	5.6
CH ₃ CO ₂ CH ₂ CH ₃	8.8

These results indicate that alumina can be added to the preparation of invention catalyst, if desired. It is of note that high selectivity to the desired hydrogenation products, methanol and ethanol,

- 32 -

are obtained even at the high rates of reaction achieved with the Pd/ZnO-Al₂O₃ catalyst.

EXAMPLE 11 - Diethyl Adipate Hydrogenation

5 A hydrogenation reaction was conducted as described in Example 8 except that diethyl adipate was used in place of DMCD and the catalyst volume was 100 cc. Operation conditions are given below:

10 Temperature - 300°C
Pressure - 1233 psig
H₂ Feed Rate - 760 sccm
Liquid Feed Rate - 189 ml/hr

Analyses of the liquid product stream gave the following results:

15 Dodecyl alcohol - 92%
Diethyl adipate - 2.2%
1,6-hexanediol - 2.8%
C₆⁺ products - 3%

20 The results show that Pd/ZnO is effective for the conversion of dibasic esters such as diethyl adipate to the corresponding diol.

EXAMPLE 12 - Methyl Oleate Hydrogenation

a. Pd/ZnO Catalyst

25 Hydrogenation of methyl oleate was carried out as described in Example 11 except that the liquid feed contained pure methyl oleate. The liquid feed rate was 68 ml/hr and the reaction temperature was 290°C. Analysis of the product mixture gave the following results.

- 33 -

Methyl oleate - 4.1 wt %
Stearyl Alcohol - 42 wt %
Oleyl Alcohol - 50 wt %

These results demonstrate the utility of Pd/ZnO
5 for the conversion of methyl oleate to a mixture of
C-18 alcohols at low pressure. Of particular note is
the fact that a significant portion of the hydrogenation
product is the unsaturated product, oleyl
alcohol. Isolation of this product is particularly
10 noteworthy in view of the fact that the material has
been subjected to reducing conditions in the presence
of a catalytic material (i.e., Pd) which is generally
quite effective for double bond hydrogenation. Thus,
hydrogenation in accordance with the present
15 invention is seen to be selective for reduction of
carbon-oxygen double bonds (i.e., carbonyl bonds)
relative to carbon-carbon double bonds.

b. Supported Catalyst Prepared as Described in
Example 1b:

20 Fifty cc's of a 5% Pd (Pd-Zn ratio of 1:2) on
SiO₂ catalyst (prepared as described in Example 3d
was loaded into a 1" tubular reactor. After catalyst
was pre-treated at 1200 psig at 300°C in a flowing
hydrogen atmosphere for 12 hours, methyl oleate feed
25 was pumped into the tubular reactor (maintained at
300°C) at the rate of about 1.4 mL/minute with a
hydrogen flow of about 744 standard cubic centimeters
per minute.

Under the above conditions, a 9% conversion of
30 methyl oleate was obtained with nearly quantitative
selectivity to a 2:1 mixture of oleyl alcohol and
stearyl alcohol.

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These results demonstrate that Pd-Zn/SiO₂ is an effective catalyst for the selective hydrogenation of methyl oleate; with the carbon-carbon unsaturation being retained in about 2/3 of the reduced product.

5 EXAMPLE 13 - Hydrogenation of Propionaldehyde

A Pd/ZnO catalyst prepared as described in Example 1a was evaluated for the vapor phase hydrogenation of propionaldehyde in a micro reactor system. Approximately 1 cc of catalyst was charged
10 to the reactor and pretreated as described in previous examples. The reaction parameters employed and results obtained were as follows:

15	Temperature	- 130°C
	Pressure	- 800 psig
	H ₂ /Aldehyde	- 4.0
	GHSV	- 30,000 h ⁻¹
	Propionaldehyde conversion	- 49.0%
20	<u>Product</u>	<u>Selectivity, wt %</u>
	CH ₃ CH ₂ CH ₂ OH	45
	2-methyl-2-pentenal	55

The results demonstrate the utility of Pd/ZnO catalyst for the conversion of propionaldehyde to propanol.

EXAMPLE 14 - Hydrogenation of Nonanal

25 A 1% Pd on ZnO catalyst prepared as described in Example 1a was evaluated for the slurry phase hydrogenation of nonanal. Nonanal (4g) was mixed with toluene (75 ml) and 1% Pd/ZnO (1 g). This mixture was placed in a stirred autoclave and heated
30 to 100°C under 100 psig hydrogen pressure. The

- 35 -

system was pressurized to 1500 psig and the mixture stirred for two hours. The autoclave was then cooled, vented and the resulting product mixture analyzed by gas chromatography (GC). For the comparative example, 1 g of a commercially available 1% Pd/Al₂O₃ was substituted for the Pd/ZnO catalyst. The results were as follows:

	<u>Catalyst</u>	<u>GC Analysis, wt %</u>		
		<u>Nonanal</u>	<u>Nonanol</u>	<u>Unknown</u>
10	1% Pd/ZnO	0.9	99.	0.0
	1% Pd/Al ₂ O ₃	28.7	60.2	11.1

Pd/ZnO exhibits substantially higher activity and selectivity than Pd/Al₂O₃ under identical conditions for the hydrogenation of nonanal.

15 The examples have been provided merely to illustrate the practice of our invention and should not be read so as to limit the scope of our invention or the appended claims in any way. Reasonable variations and modifications, not departing from the essence and spirit of our invention, are contemplated to be within the scope of patent protection desired and sought.

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Claims

We Claim:

1. A method for preparing high activity, low pressure hydrogenation catalysts comprising palladium and zinc on a support, said method comprising:
 - (a) contacting said support with at least one of zinc or a reducible compound thereof and palladium or a reducible compound thereof;
 - 10 (b) optionally calcining the resulting palladium and/or zinc treated support in the presence of an oxygen-containing gas at a temperature in the range of 200 up to 400°C for a time sufficient to activate said palladium and/or said zinc component;
 - 15 (c) where palladium is employed in step (a), optionally contacting said palladium-treated support with a reducing atmosphere under conditions sufficient to cause reduction of at least a portion of the palladium to less than the +2 oxidation state;
 - 20 (d) optionally contacting said support again with at least one member selected from the group consisting of palladium or a reducible compound thereof and zinc or a reducible compound thereof, with the proviso that said support is ultimately contacted with both palladium and zinc;
 - 25 (e) optionally calcining the resulting palladium and zinc treated support in the presence of an oxygen-containing gas at a temperature in
 - 30

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the range of 200° up to 400°C for a time sufficient to activate said palladium and said zinc component; and thereafter

(f) contacting the zinc and palladium-treated support with a reducing atmosphere under conditions sufficient to cause reduction of at least a portion of the palladium to less than the +2 oxidation state.

2. A method in accordance with Claim 1 wherein said contacting step (a) comprises contacting said support with palladium or a reducible compound thereof; wherein optional step (b) is omitted; wherein step (c) comprises contacting said palladium-treated support with a reducing atmosphere under conditions sufficient to form highly dispersed, supported zerovalent palladium; wherein optional step (d) comprises contacting said supported zerovalent palladium with zinc or a reducible compound thereof; and thereafter; optionally carrying out steps (e) and (f).

3. A method in accordance with Claim 1 wherein the quantity of said palladium employed is in the range of 0.01 up to 20 wt %, calculated as the metal and based on the total weight of palladium, zinc and support.

4. A method in accordance with Claim 3 wherein the atomic ratio of Pd to Zn falls within the range of about 0.01 up to 10.

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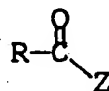
5. A method in accordance with Claim 1 wherein said support has a surface area of at least about $1 \text{ m}^2/\text{g}$.
6. A method in accordance with Claim 5 wherein said support is selected from the group consisting of:
 - SiO_2
 - TiO_2
 - C,
 - Rare earth oxides,
 - Al_2O_3 ,as well as mixtures of any two or more thereof.
7. A method in accordance with Claim 5 wherein said support is silica.
8. A method in accordance with Claim 7 wherein the quantity of palladium employed is in the range of 0.5 up to 6 weight %, calculated as the method and based on the total weight of palladium, zinc, and support.
9. A method in accordance with Claim 8 wherein the atomic ratio of Pd to Zn falls within the range of about 0.2 up to 5.0.
10. A method in accordance with Claim 1 wherein said calcination is carried out for a time in the range of about 0.5 up to 8 hours.
11. A method in accordance with Claim 2 wherein said reducing atmosphere comprises active hydrogen.
12. A method in accordance with Claim 11 wherein said contacting with a reducing atmosphere is carried

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out at a temperature in the range of 25 up to 400°C for a time sufficient to form highly dispersed, supported zerovalent palladium.

13. A method in accordance with Claim 1 wherein said
5 reducing atmosphere comprises active hydrogen.
14. A method in accordance with Claim 13 wherein said
contacting with a reducing atmosphere is carried
out at a temperature in the range of 25 up to
400°C for a time sufficient to reduce at least a
10 portion of the palladium to less than the +2
oxidation state.
15. The catalyst prepared by the method of Claim 1.
16. The catalyst prepared by the method of Claim 2.
17. The catalyst prepared by the method of Claim 6.
- 15 18. The catalyst prepared by the method of Claim 9.
19. A process for the low pressure hydrogenation of
carbonyl-containing compounds to produce the
corresponding alcohol, wherein said carbonyl-
containing compounds have the structure:

20



wherein R is a $\text{C}_1\text{-C}_{20}$ alkyl or substituted
alkyl radical; or

25

a $\text{C}_2\text{-C}_{20}$ alkenyl or alkynyl radical or a
substituted derivative thereof;

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wherein said substituted groups include ethers, amines, additional carbonyl groups, aryl groups, hydroxyl groups and alkoxy groups; and

Z=H,

5 R', wherein R' is defined the same as R, and is selected independently of R,

OR', wherein R' is as defined above,

X, wherein X is any one of the halogens, or

10 NR''₂, wherein each R'' is independently selected from H or R';

with the proviso that R and Z can be joined as part of a polymethylene or hydrocarbyl- or heteroatom-substituted polymethylene radical,

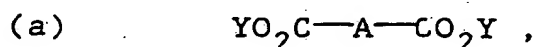
15 poly-carbonyl analogs of such carbonyl-containing compounds; and

mixtures of any two or more thereof;

20 said process comprising contacting said carbonyl-containing compounds with an optionally supported palladium and zinc containing catalyst comprising 0.01 up to 20 wt % palladium calculated as the metal and based on the total weight of catalyst; and wherein the atomic ratio of Pd to Zn falls within the range of about 0.01 up to 10; wherein said contacting is carried out in the presence of
25 hydrogen under hydrogenation conditions.

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20. A process in accordance with Claim 19 wherein said contacting is carried out in the further presence of in the range of 0.01 up to 2.0 wt % water, based on the total weight of reactants and solvent charged to the reactor.
21. A process in accordance with Claim 19 wherein said hydrogenation conditions comprise a temperature in the range of 25 up to 400°C, and a pressure in the range of 100 up to 10,000 psig.
22. A process in accordance with Claim 19 wherein the hydrogen partial pressure falls within the range of 100 up to 10,000 psig.
23. A process in accordance with Claim 19 wherein said hydrogenation conditions comprise a temperature in the range of 100 up to 290°C and a pressure in the range of 100 up to 2500 psig.
24. A process in accordance with Claim 19 wherein the liquid hourly space velocity falls within the range of about 0.01 up to 100 h⁻¹.
25. A process in accordance with Claim 19 wherein the weight ratio of carbonyl-containing compound to catalyst falls within the range of 1:1 up to 10,000:1.
26. A process in accordance with Claim 19 wherein the carbonyl-containing compound is selected from the group consisting of:



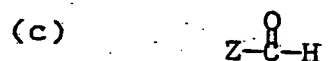
- 42 -

wherein A is an alkylene moiety, an alkenylene moiety, or an alkynylene moiety having 1 up to 20 carbon atoms, or substituted derivative thereof, or a cycloalkyl or cycloalkenyl moiety having 4-12 carbon atoms or substituted derivative thereof; and wherein each Y is independently a C₁ up to C₁₂ alkyl, alkenyl or alkynyl radical or substituted derivative thereof;



wherein B is an alkyl, alkenyl or alkynyl radical, or substituted derivative thereof, having 1 up to 20 carbon atoms; and

wherein Y is defined as above;



wherein Z is an alkyl, alkenyl or alkynyl radical having 1 up to 20 carbon atoms or substituted derivatives thereof; and

mixtures of any two or more thereof.

27. A process in accordance with Claim 26 wherein the carbonyl-containing compound comprises a dialkyl adipate.

28. A process in accordance with Claim 27 wherein said alkyl radical has in the range of 1 up to 6 carbon atoms.

29. A process in accordance with Claim 26 wherein the carbonyl-containing compound comprises a dialkyl cyclohexanedicarboxylate.

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30. A process in accordance with Claim 29 wherein said alkyl radical has in the range of 1 up to 6 carbon atoms.
- 5 31. A process in accordance with Claim 26 wherein the carbonyl-containing compound is selected from the group consisting of an alkyl oleate, an alkyl stearate, an alkyl linoleate, an alkyl linolenate, an alkyl α -eleostearate, an alkyl β -eleostearate, and mixtures of any two or more thereof.
- 10 32. A process in accordance with Claim 31 wherein said alkyl radical has in the range of 1 up to 6 carbon atoms.
- 15 33. A process in accordance with Claim 26 wherein the carbonyl-containing compound comprises a dialkyl butanedicarboxylate.
34. A process in accordance with Claim 33 wherein said alkyl radical has in the range of 1 up to 6 carbon atoms.
- 20 35. A process in accordance with Claim 26 wherein the carbonyl-containing compound comprises a glycerol ester.
- 25 36. A process in accordance with Claim 35 wherein said alkyl radical has in the range of 1 up to 6 carbon atoms.
37. A process in accordance with Claim 26 wherein the carbonyl-containing compound comprises a dialkyl glutarate.

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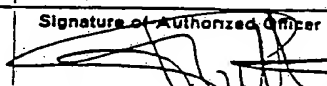
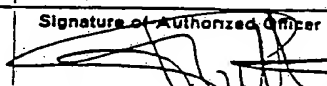
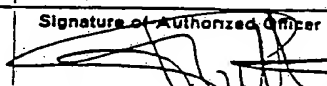
38. A process in accordance with Claim 37 wherein said alkyl radical has in the range of 1 up to 6 carbon atoms.
- 5 39. A process in accordance with Claim 26 wherein the carbonyl-containing compound is selected from the group consisting of dialkyl fumarates, succinates, maleates, and mixtures of any two or more thereof.
- 10 40. A process in accordance with Claim 39 wherein said alkyl radical has in the range of 1 up to 6 carbon atoms.
41. A process in accordance with Claim 26 wherein the carbonyl-containing compound comprises an alkyl decanoate.
- 15 42. A process in accordance with Claim 41 wherein said alkyl radical has in the range of 1 up to 6 carbon atoms.
- 20 43. A process in accordance with Claim 26 wherein the carbonyl-containing compound comprises an alkyl dodecanoate.
44. A process in accordance with Claim 43 wherein said alkyl radical has in the range of 1 up to 6 carbon atoms.
- 25 45. A process in accordance with Claim 26 wherein the carbonyl-containing compound is selected from the group consisting of alkyl acetates, propionates, butyrates, valerates, caproates, and mixtures of any two or more thereof.

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46. A process in accordance with Claim 45 wherein said alkyl radical has in the range of 1 up to 6 carbon atoms.

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US 88/02576

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁴ According to International Patent Classification (IPC) or to both National Classification and IPC IPC ⁴ : B 01 J 23/60; B 01 J 37/00; C 07 C 29/14; C 07 C 29/136																	
II. FIELDS SEARCHED <div style="text-align: center; margin-top: 10px;">Minimum Documentation Searched ⁷</div> <table style="width: 100%; border: none;"> <tr> <td style="width: 30%; border: none;">Classification System</td> <td style="border: none;">Classification Symbols</td> </tr> <tr> <td style="border: none; padding: 5px;">IPC⁴</td> <td style="border: none; padding: 5px;">B 01 J; C 07 C</td> </tr> </table> <div style="text-align: center; margin-top: 10px;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸</div>			Classification System	Classification Symbols	IPC ⁴	B 01 J; C 07 C											
Classification System	Classification Symbols																
IPC ⁴	B 01 J; C 07 C																
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹ <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 10%;">Category ⁹</th> <th style="width: 70%;">Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²</th> <th style="width: 20%;">Relevant to Claim No. ¹³</th> </tr> </thead> <tbody> <tr> <td style="text-align: center; vertical-align: top;">A</td> <td>FR, A, 1392376 (SNAM) 1 February 1965 --</td> <td></td> </tr> <tr> <td style="text-align: center; vertical-align: top;">A</td> <td>US, A, 2818393 (LEFRANCOIS) 31 December 1957 --</td> <td></td> </tr> <tr> <td style="text-align: center; vertical-align: top;">A</td> <td>US, A, 4052467 (MILLS et al.) 4 October 1977 --</td> <td></td> </tr> <tr> <td style="text-align: center; vertical-align: top;">P, A</td> <td>EP, A, 0241760 (HENKEL) 21 October 1987 -----</td> <td></td> </tr> </tbody> </table>			Category ⁹	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³	A	FR, A, 1392376 (SNAM) 1 February 1965 --		A	US, A, 2818393 (LEFRANCOIS) 31 December 1957 --		A	US, A, 4052467 (MILLS et al.) 4 October 1977 --		P, A	EP, A, 0241760 (HENKEL) 21 October 1987 -----	
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<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>¹⁰ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p> </div> </div>																	
IV. CERTIFICATION <table style="width: 100%; border: none;"> <tr> <td style="width: 50%; border: none;">Date of the Actual Completion of the International Search</td> <td style="width: 50%; border: none;">Date of Mailing of this International Search Report</td> </tr> <tr> <td style="border: none; text-align: center;">6th December 1988</td> <td style="border: none; text-align: center;">22 DEC 1988</td> </tr> <tr> <td style="border: none;">International Searching Authority</td> <td style="border: none;">Signature of Authorized Officer</td> </tr> <tr> <td style="border: none; text-align: center;">EUROPEAN PATENT OFFICE</td> <td style="border: none; text-align: center;">  P.C.G. VAN DER PUTTEN </td> </tr> </table>			Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	6th December 1988	22 DEC 1988	International Searching Authority	Signature of Authorized Officer	EUROPEAN PATENT OFFICE	 P.C.G. VAN DER PUTTEN							
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ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

US 8802576
SA 24023

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 15/12/88. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
FR-A- 1392376		DE-C- 1213839 NL-A- 6405225 BE-A- 647710 LU-A- 46049 GB-A- 1024318 CH-A- 438269	30-04-75 11-11-64 09-11-64 09-11-65
US-A- 2818393		None	
US-A- 4052467	04-10-77	None	
EP-A- 0241760	21-10-87	DE-A- 3610698	01-10-87

